

Purdue MSE597G Lectures on Molecular Dynamics simulations of materials

Lecture 3 Statistical Mechanics II

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Molecular Dynamics simulations

Introduction

- What is molecular dynamics (MD)? Examples of current research
- Why molecular dynamics?

Part 1: the theory behind molecular dynamics

- Basic ideas & algorithms
- Brief introduction to the physics necessary to run & understand MD

Part 2: total energy and force calculations

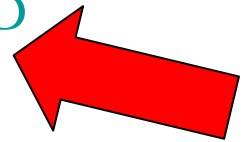
- Quantum mechanical origin of atomic interactions
- Inter-atomic potentials: “averaging electrons out”

Part 3: advanced techniques, mesodynamics, verification and validation

- MD in under isothermal and isobaric conditions
- Coarse grain approaches and dynamics with implicit degrees of freedom
- Before you perform production runs

•Tutorial to perform MD simulations using the nanoMATERIALS simulation tool at the nanoHUB

•Homework exercises



Various important ensembles

Microcanonical (NVE)

Canonical (NVT)

Isobaric/isothermal (NPT)

Probability distributions

$$P(\{r_i\}, \{p_i\}) = \frac{1}{\Omega(E, V, N)}$$

$$P(\{r_i\}, \{p_i\}) = \frac{e^{-\frac{H(\{r_i\}, \{p_i\})}{kT}}}{Z(T, V, N)}$$

$$P(\{r_i\}, \{p_i\}, V) = \frac{e^{-\frac{1}{kT}[H(\{r_i\}, \{p_i\}) - PV]}}{Z_P(T, P, N)}$$

$$\Omega(E, V, N) = \sum_{micro} \delta(E - H(\{r_i\}, \{p_i\}))$$

$$Z(T, V, N) = \sum_{micro} e^{-\frac{E}{kT}}$$

$$Z_P(T, P, N) = \sum_V \sum_{micro} e^{-\frac{E - PV}{kT}}$$

Free energies (atomistic \leftrightarrow macroscopic thermodynamics)

$$S = k \log \Omega(E, V, N)$$

$$F(T, V, N) = -kT \log Z$$

$$G(T, P, N) = -kT \log Z_p$$

Canonical ens.: equipartition of energy

Consider a variable that appears squared in the Hamiltonian:

$$H(\{r_i\}, \{p_i\}) = \lambda p_1^2 + V(\{r_i(t)\}) + \sum_{i=2}^{3N} \frac{p_i(t)^2}{2m_i} = \lambda p_1^2 + H'$$

$$\langle \lambda p_1^2 \rangle = \frac{\int d^{3N} p d^{3N} p \lambda p_1^2 e^{-\frac{H(\{r_i\}, \{p_i\})}{kT}}}{\int d^{3N} p d^{3N} p e^{-\frac{H(\{r_i\}, \{p_i\})}{kT}}} = \frac{\int d^{3N} p d^{3N-1} p e^{-\frac{H'}{kT}} \int dp_1 \lambda p_1^2 e^{-\frac{\lambda p_1^2}{kT}}}{\int d^{3N} p d^{3N-1} p e^{-\frac{H'}{kT}} \int dp_1 e^{-\frac{\lambda p_1^2}{kT}}}$$

Change of variable: $\frac{\lambda p_1^2}{kT} = x^2$ $dp_1 = \frac{kT}{\lambda} dx$

$$\langle \lambda p_1^2 \rangle = \frac{\frac{(kT)^2}{\lambda} \int dx x^2 e^{-x^2}}{\frac{kT}{\lambda} \int dx e^{-x^2}} = \frac{1}{2} kT$$

Equipartition of energy: Any degree of freedom that appears squared in the Hamiltonian contributes $1/2kT$ of energy

Equipartition of energy: MD temperature

$$\langle K \rangle = \frac{3N}{2} kT$$

In most cases c.m. motion is set to zero at time zero (constant of motion → it remains zero)

$$\langle K \rangle = \frac{3N-3}{2} kT$$

Often angular momentum is zeroed (and remains zero)

$$\langle K \rangle = \frac{3N-6}{2} kT$$

Temperature is related to **average** kinetic energy. Instantaneous temperature:

$$K(t) = \frac{N_{eff}}{2} kT(t)$$

Fluctuations

Fluctuations from equilibrium are also related to materials properties

$$\langle \delta A^2 \rangle = \frac{1}{\tau} \int_0^\tau [A(t) - \langle A \rangle]^2 dt = \langle A^2 \rangle - \langle A \rangle^2$$

Specific heat:

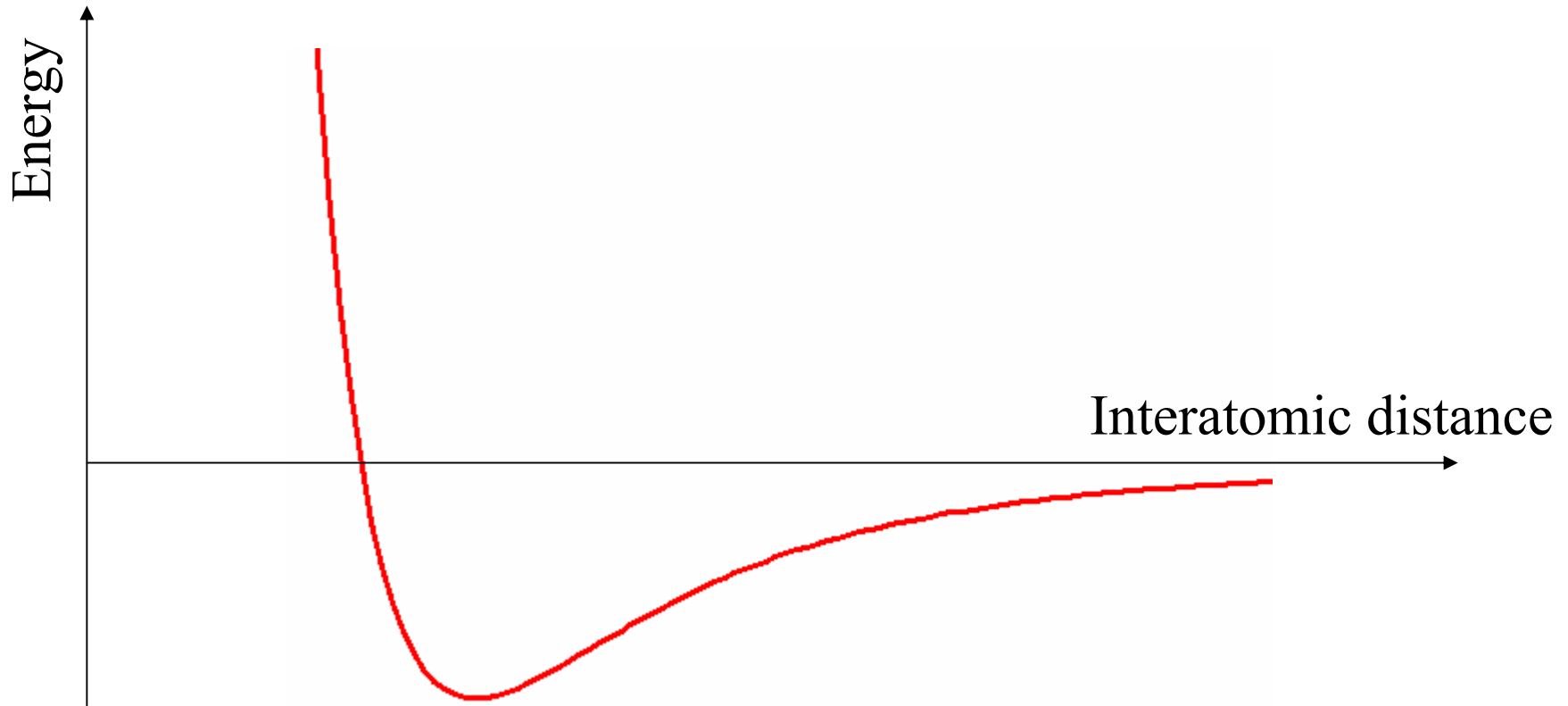
$$C_V = \left. \frac{\partial E}{\partial T} \right|_{NVT} \qquad \langle \delta H^2 \rangle_{NVT} = kT^2 C_V$$

Compressibility:

$$\beta_V = \left. \frac{1}{V} \frac{\partial V}{\partial P} \right|_{NVT} \qquad \langle \delta V^2 \rangle_{NPT} = k \langle V \rangle T \beta_T$$

Quantum effects

When does classical mechanics for atoms stop working?



Temperature at which quantum effects kick in depends on frequency

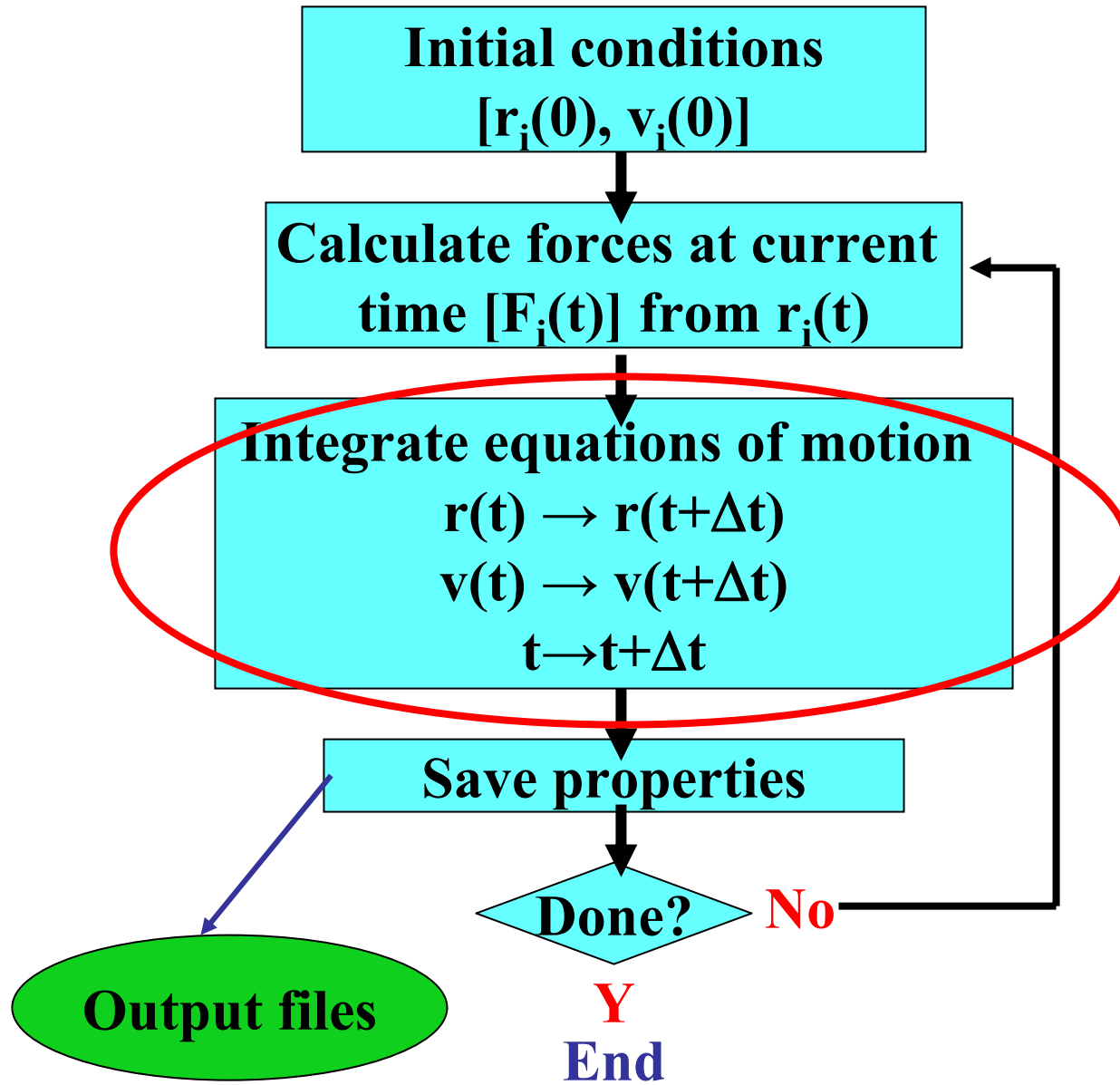
$kT \gg \hbar\omega$ Classical regime

$kT \sim < \hbar\omega$ Quantum regime

Statistical mechanics: further reading

- Kerson Huang: “*Statistical Mechanics*”
- Landau and Lifshitz: “*Course of Theoretical Physics Volume 5: Statistical Physics*”
- Balescu: “*Equilibrium and nonequilibrium statistical mechanics*”

How do we numerically integrate the equations of motion?



Integrating the equations of motion

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i}$$

$$\dot{\vec{p}}_i = \vec{F}_i$$

Verlet algorithm: Taylor expansion of positions with time

$$r_i(t + \Delta t) = r_i(t) + \dot{r}_i(t)\Delta t + \frac{1}{2}\ddot{r}_i(t)\Delta t^2 + \frac{1}{6}\dddot{r}_i(t)\Delta t^3 + \mathcal{O}(\Delta t^4)$$

$$r_i(t - \Delta t) = r_i(t) - \dot{r}_i(t)\Delta t + \frac{1}{2}\ddot{r}_i(t)\Delta t^2 - \frac{1}{6}\dddot{r}_i(t)\Delta t^3 + \mathcal{O}(\Delta t^4)$$

Sum two equations:

Verlet algorithm: various equivalent formulations

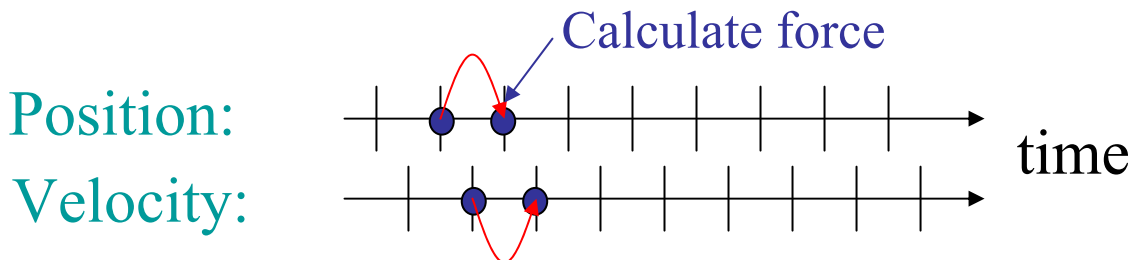
Velocity Verlet: $\left\{ \begin{array}{l} p_i\left(t + \frac{1}{2}\Delta t\right) = p_i(t) + \frac{1}{2}F_i(t)\Delta t \\ r_i(t + \Delta t) = r_i(t) + \frac{p_i\left(t + \frac{1}{2}\Delta t\right)}{m_i}\Delta t \\ p_i(t + \Delta t) = p_i\left(t + \frac{1}{2}\Delta t\right) + \frac{1}{2}F_i(t + \Delta t)\Delta t \end{array} \right.$

Advance p half step

Advance r full step
(with p half step ahead)

Advance p half step
(with F at $t + \Delta t$)

Leap-Frog Verlet: $\left\{ \begin{array}{l} r_i\left(t + \frac{1}{2}\Delta t\right) = r_i\left(t - \frac{1}{2}\Delta t\right) + v_i(t)\Delta t \\ v_i(t + \Delta t) = v_i(t) + \frac{1}{m_i}F_i\left(t + \frac{1}{2}\Delta t\right) \end{array} \right.$



Verlet algorithm: features and advantages

- Exactly time reversible
 - If velocities are reversed at a given time the algorithm traces back its steps
- Symplectic
 - Conserves volume in phase space (as Hamiltonian dynamics does)



- No long-term energy drifts
- The trajectory stays very close to the constant energy hypersurface in phase space

Remember: $S = k \log \Omega(E, V, N)$

Molecular Dynamics simulations

Introduction

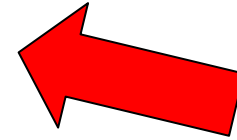
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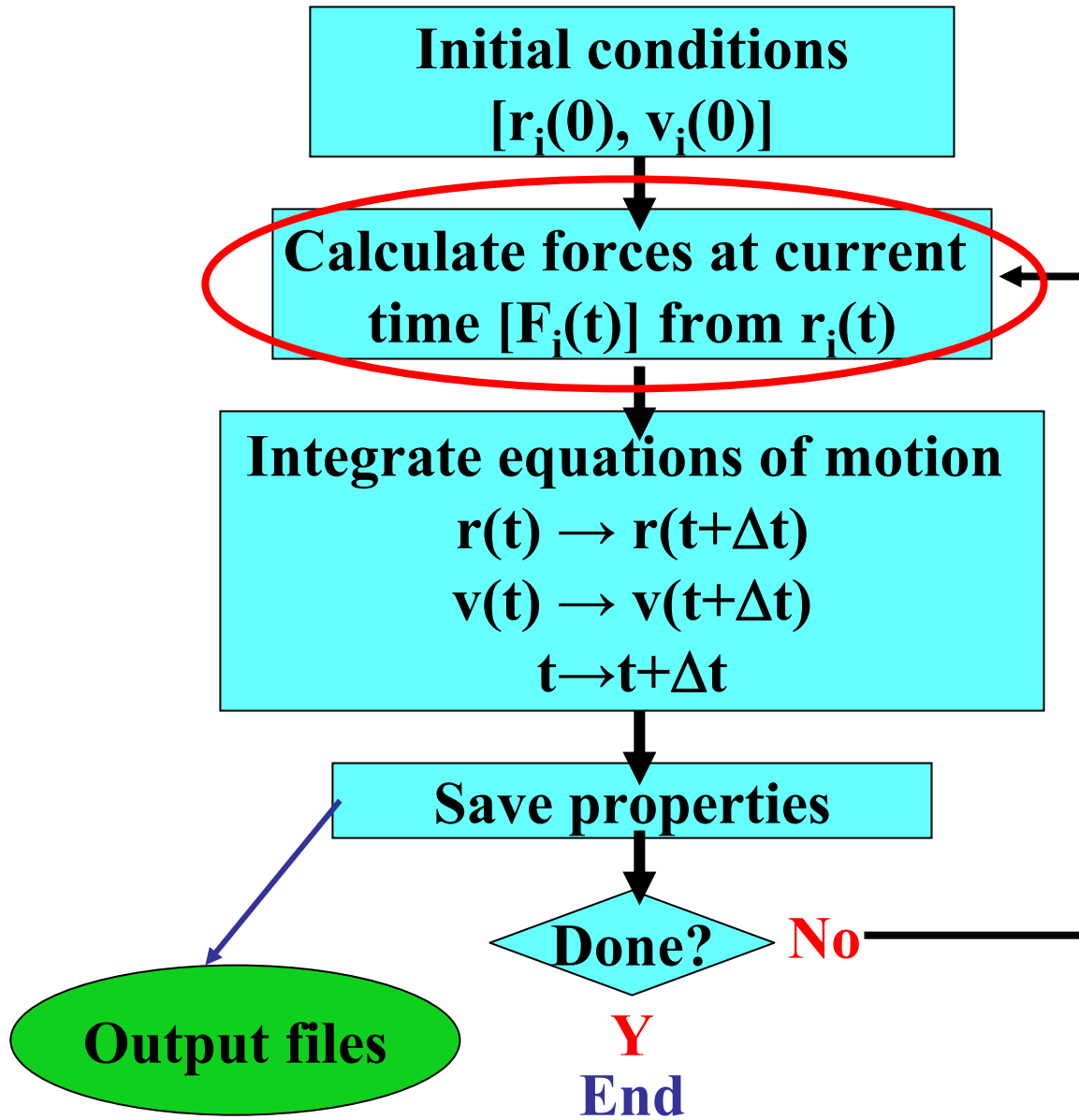


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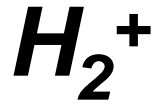
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How do we calculate atomic forces?



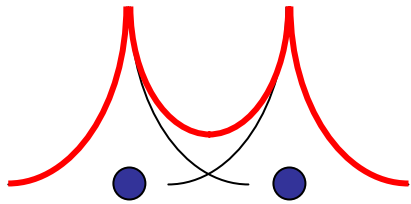
The simplest molecule:



proton ● ● electron (e⁻)
 ● proton

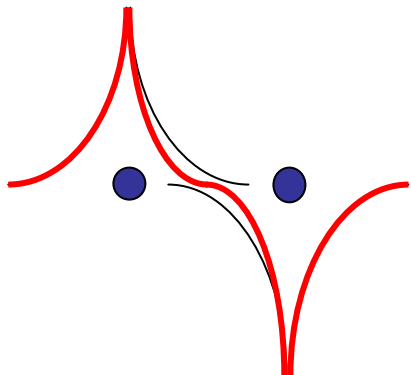
Molecular wave function as linear combination of atomic orbitals (LCAO)

$$\psi_{sym}(\vec{r}) = \frac{1}{\sqrt{2}}(\psi_L(\vec{r}) + \psi_R(\vec{r}))$$

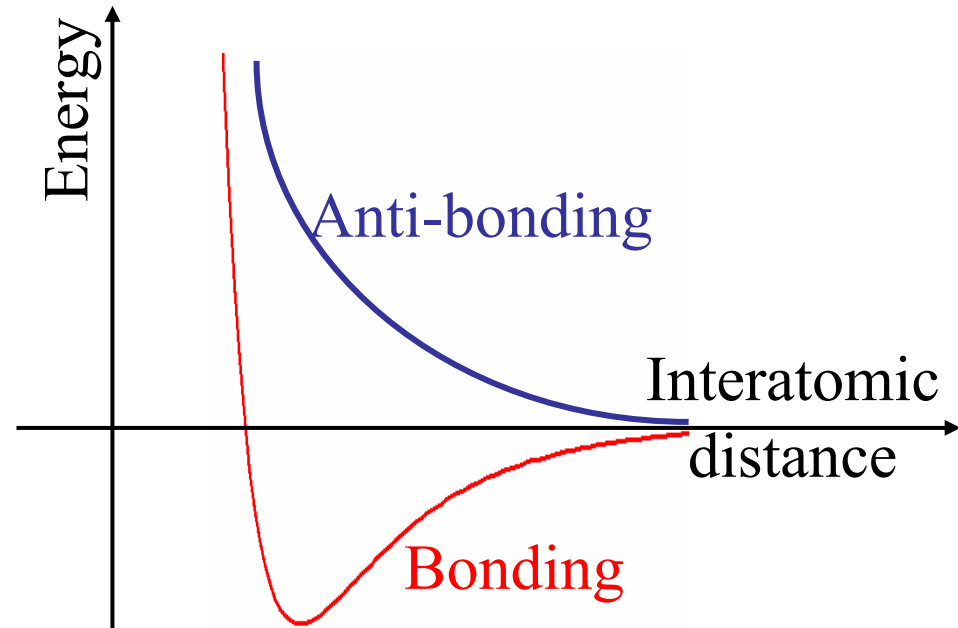


- K.E. good
- P.E. not so good
- **Bonding**

$$\psi_{asym}(\vec{r}) = \frac{1}{\sqrt{2}}(\psi_L(\vec{r}) - \psi_R(\vec{r}))$$

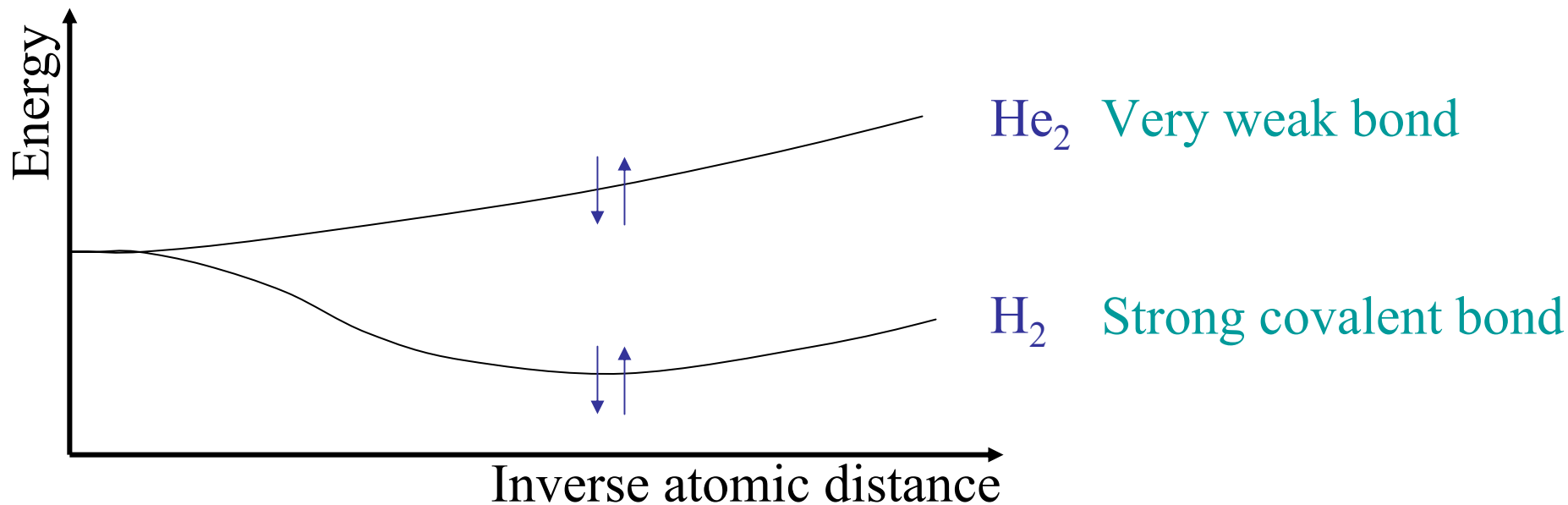


- K.E. not so good
- P.E. good
- **Anti-bonding**



Covalent and non-bond interactions

IA																		VIIIA
H	IIA											IIIA	IVA	VA	VIA	VIIA	He	
Li	Be											B	C	N	O	F	Ne	
Na	Mg	IIIB	IVB	VB	VIB	VII B	VIII	VIII	VIII	IB	IIB	Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	



How can we compute interatomic potential?

- *Ab initio* electronic structure methods
 - Hartree Fock, Density Functional Theory
 - Quantum Monte Carlo
 - Very accurate but computationally intensive
(applicable to small systems – 100s-1000s atoms)

- Interatomic potentials:

$$V(\{r_i\}) = V_{\text{cov/met}}(\{r_i\}) + V_{\text{electr}}(\{r_i\}) + V_{\text{vdW}}(\{r_i\})$$

Parameterized to describe specific materials

- *Ab initio* data
- Experiments